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RESEARCH MEMORANDUM

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THE REACTION PRODUCTS OF SODIUM HYDROXIDE

AND CHROMIUM METAL

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THERMAL ANALYSIS OF SODIUM HYDROXIDE CONTAINING THE REACTION

PRODUCTS OF SODIUM HYDROXIDE AND CHROMIUM METAL

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SUMMARY

Cooling curves were established for melts of sodium hydroxide that had been reacted with up to 20-percent-by-weight additions of chromium metal for varying times at 820° C (1500° F). For any given time at temperature, the depression of the freezing point of the hydroxide was increased with increasing chromium concentration. This depression diminished with increasing reaction time. A eutectic of the hydroxide and some reaction product was observed at 289°±3° C. This eutectic was not evident at low chromium concentrations and disappeared at long reaction times. These results are explained on the assumption that gradual loss of the initial reaction products of chromium by some further reaction results in their removal from the melt.

INTRODUCTION

The beneficial action of chromium metal in reducing mass transfer in a sodium hydroxide – nickel system at high temperature (820° C or 1500° F) has been established (refs. 1 and 2). It is now desirable to know more about the chemical reactions taking place between the hydroxide and chromium and how these reactions or their products affect the transfer process. It is also necessary to know how they affect the properties of the bulk unreacted sodium hydroxide. In general, there are three ways to approach the study of such a system: (1) examination of the molten and gaseous products at some high temperature, perhaps the reaction temperature; (2) examination of the solidified melt; and

(3) examination of the solutions and residues formed when the solidified melt is dissolved in appropriate solvents. It is probable that information gathered from all these sources will be needed to understand the reactions and their effects on the mass-transfer process.

Presented in this report are the results of the thermal analysis of sodium hydroxide reacted in nickel containers under static conditions at a reaction temperature of 820° C (1500° F) for various times and with varying amounts of added chromium metal. In particular, the effect of the reaction products on the freezing point of sodium hydroxide is given, and an explanation for the changes noted in the solidifying melt is presented.

<center>EXPERIMENTAL PROCEDURES</center>

The fabrication of nickel containers, the handling and treatment of sodium hydroxide prior to heating to reaction temperature, and the procedure for adding chromium metal (in the form of 325 mesh powder) have been described previously (ref. 3). The total weight of material placed in each container was 13.00 grams (±1.0 percent error in the weight of sodium hydroxide). The high-temperature furnace, its controls, and a holder for the nickel containers, which were used to carry out the reaction at 820° C, are also described in reference 3. After the reaction proceeded for a given length of time, the containers were removed from the furnace and quenched. Before each cooling run was made, the thermocouples were removed and the heavy oxide coating, which forms on the surface of the container at the high temperature, was ground off until the base metal was exposed. A new thermocouple was spot welded to the side of each container 1/4 inch from the bottom.

Cooling curves for the various melts were then made in the following manner: The containers were suspended in the center of a tube furnace, 12 inches long, with a 3-inch inside diameter (fig. 1). The furnace was heated until the container reached a temperature of about 450°±20° C. The power to the furnace was then cut off, and the furnace and container were allowed to cool. The thermal electromotive force of the thermocouple was recorded on a recording potentiometer. At the end of each run, the bucking potential supplied to the thermocouple (to keep the emf within the range of the recorder) and the recorder calibration was checked with another potentiometer. A typical cooling curve, characteristic of sodium hydroxide with no additive, is shown in figure 2.

<center>RESULTS AND DISCUSSION</center>

All observed transition temperatures fell within the range of 285° to 325° C. The specific values of these temperatures are listed in table I. All melts with a chromium addition of up to 15 percent by

weight exhibit a transition, b, at $296°±2°$ C. Another transition temperature, a, ranging from $321°$ to $294°$ C appears to decrease with increasing chromium concentrations for any given time at reaction temperature. A third transition, c, appears in the range $286°$ to $292°$ C for melts containing 10 percent or more chromium. As is shown in the cooling curves in figure 3, the magnitude of these breaks is much smaller than for transitions a or b.

Sodium hydroxide is known to undergo a solid-phase transition, $NaOH_\alpha \rightleftharpoons NaOH_\beta$, at a temperature $20°$ to $30°$ C below its freezing point. Values found in the literature for both the freezing point and the $\alpha \rightleftharpoons \beta$ transition point of the pure hydroxide are shown in the following table:

Freezing point, °C	Transition point, °C	Ref.
318.4	299.6	4
310	290	5
328	295	6
320	294	7

The observed values for these temperatures in sodium hydroxide with no additive are shown in table I. Their average values are $320°$ and $296°$ C.

Since each cooling curve was made with different, uncalibrated thermocouples, the absolute values of the temperatures are uncertain. However, the temperature differences between transitions for any given run would not be affected by this, nor would they be affected by differences in the welding of each couple. The temperature differences ΔT between transitions a and b, that is, between the freezing point and the $\alpha \rightleftharpoons \beta$ solid-phase transition point, are also listed in table I. They provide a better indication of the effect of reaction products on the freezing point of sodium hydroxide than do the values of the temperatures themselves. At some chromium concentration greater than 12 percent, the freezing point is lowered to a value less than the $\alpha \rightleftharpoons \beta$ solid-phase transition temperature. This is the case for 15- and 20-percent-chromium additions. The general effect of chromium additions on the freezing point is a lowering of its value with increasing amounts of additive. It should be noted, however, that this effect diminishes with time at reaction temperature (shown graphically in figs. 3 and 4).

The third transition temperature, c, $(289°±3°$ C) is not seen at chromium concentrations of 5 percent or less. In addition, it disappears after long reaction times at higher concentrations. The most probable explanation for this behavior is that a eutectic of sodium hydroxide and reaction products containing chromium freezes out at this temperature. Under such a condition, the amount of eutectic formed would depend on the amount of reaction product present in the melt. Thus, at low

initial chromium concentrations or after long reaction times, the amount would be small and its freezing out might not be detected by the relatively crude techniques employed in this study.

Unreacted chromium metal or insoluble products resulting from the reaction of chromium with sodium hydroxide could not affect the freezing point of the hydroxide. It is also apparent from the observed data for sodium hydroxide with no additive that any reaction products from the mass-transfer process do not affect its freezing point. Its value remains unchanged after 240 hours at reaction temperature even though mass transfer after such long times is very extensive, as can be seen in X-ray shadowgraphs of the containers (fig. 5).

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Another investigation at this laboratory indicates that water solutions of melts reacted for up to 80 hours contain chromium in the +6 valence state (chromate ion) and a small amount in the +3 valence state (chromite ion). The water-insoluble residue contains the bulk of the reacted chromium, and is primarily some insoluble chromite compound such as sodium chromite (Na_3CrO_3) or chromic oxide (Cr_2O_3). With increasing reaction times for the melts, the water solutions contain increasing amounts of chromate ion. These observations indicate that the initial reaction of chromium metal with sodium hydroxide results in the oxidation of the metal to the +3 valence state. Further reactions with the hydroxide (or some other component in the system) oxidize the +3 valence state to the +6 valence state, that is, result in the formation of a chromate compound.

If it is assumed that the main reactions taking place in the melt are those leading to the oxidation of chromium to its highest valence state and that the by-products of the reactions play an unimportant role, the observed effects on the freezing-point depression can be accounted for in either of the following ways:

(1) The chromite compound is completely soluble and the chromate is insoluble; thus the freezing-point depression is decreased as the chromite is oxidized to chromate.

(2) Either or both the chromite and chromate compounds which are initially soluble in the melt are used up by some other process, for example, by precipitation as insoluble oxides. The freezing-point depression then decreases as the compounds are removed from the melt.

Without evidence to the contrary, the most probable cause for the decrease in the freezing-point depression would be removal of the chromium compounds by some process such as suggested in item (2).

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It is this process (item (2)) that evokes the most interest with regard to the effect of chromium additives on the mass-transfer process. Other experiments carried out at this laboratory indicate that the initial reaction of chromium metal with sodium hydroxide is accompanied by the evolution of hydrogen gas. Using the rate of gas evolution as a measure of the rate of this initial process showed that the bulk of chromium metal was nearly all reacted within the first few hours at reaction temperature; therefore the reaction should be nearly complete within the first 24 hours. (This does not apply to those cases described herein where part of the metal was added in the form of lumps. For a given mass of metal, the large difference in surface area between lumps and 325 mesh powder would undoubtedly affect the rate of the initial reaction.) It has also been shown that the effects of chromium additions on reducing mass transfer persist much longer than 24 hours (refs. 1 and 2). Thus one is lead to speculate on the proposition that the reactions leading to the removal or using of the initial chromium products are those related to the reduction in the mass-transfer process. The next obvious step is the identification of those compounds that persist for long times and cause the change in the freezing-point depression of the melt. They must play an important role in the protective action of the sodium hydroxide - nickel system.

Lewis Flight Propulsion Laboratory
    National Advisory Committee for Aeronautics
        Cleveland, Ohio, August 10, 1955

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TABLE I. - TRANSITION TEMPERATURES OBSERVED FOR VARIOUS

SODIUM HYDROXIDE MELTS

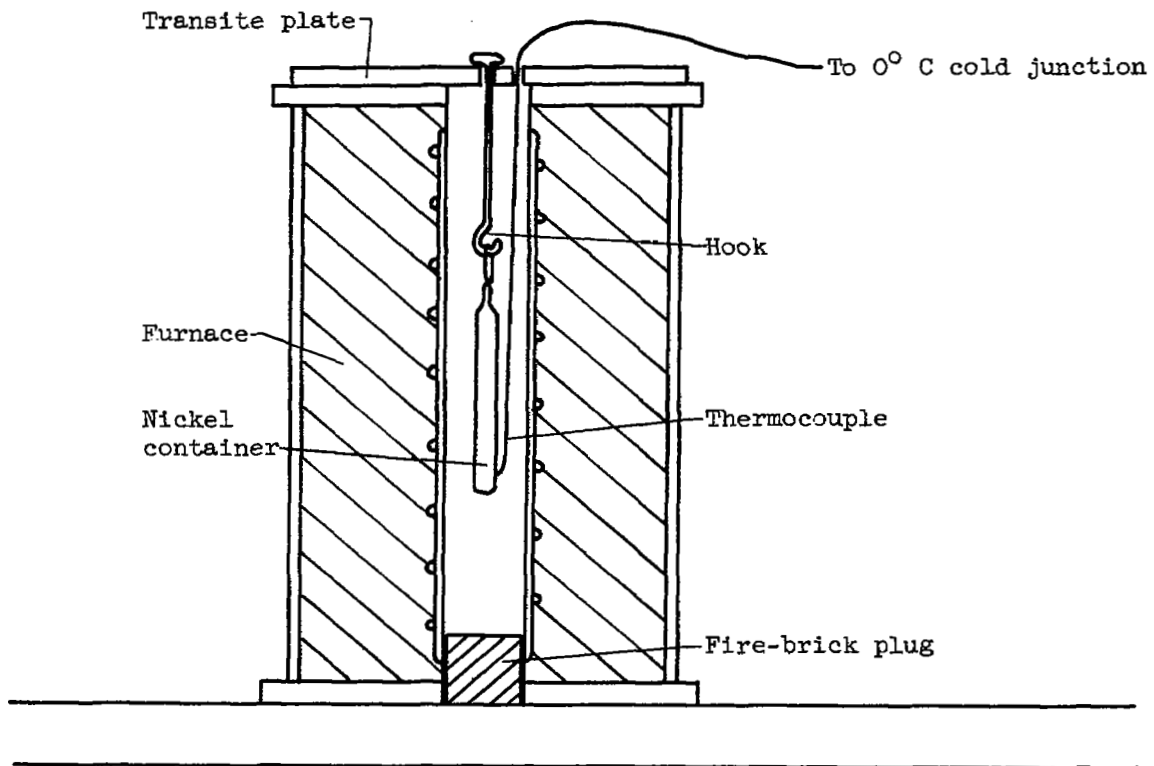| Container	Chromium, percent by weight	Time at reaction temperature, hr	Transition temperatures, $^{\circ}C$			Temperature difference, ΔT, $^{\circ}C$ (a-b)
			Freezing point, a	Solid phase, b	Eutectic point, c	
W-9	0	0	320	296	---	24
		23	321	296	---	25
		55	319	295	---	24
		103	321	297	---	24
		205	318	294	---	24
		245	321	297	---	24
W-10	5.8	23	315	298	---	17
		55	315	296	---	19
		103	317	295	---	21
		205	317	294	---	23
W-11	10.0	23	306	297	287	9
		55	306	297	291	9
		103	310	297	290	13
		205	312	295	---	17
		245	316	297	---	19
W-12	10.0	23	304	296	286	8
		55	304	296	290	8
		103	308	296	287	12
		205	312	296	---	16
		245	316	297	---	19
B	1.3	144	319	296	---	23
W-2	0	96	319	296	---	23
W-4	5.8	96	317	295	---	22
W-7	12.0	96	302	296	289	6
W-13	0	240	319	296	---	23
W-14	10.0	240	314	297	---	17
W-15	15.0	240	296	---	292	--
W-16	20.0	240	294	---	290	--
Av. value			296		289	

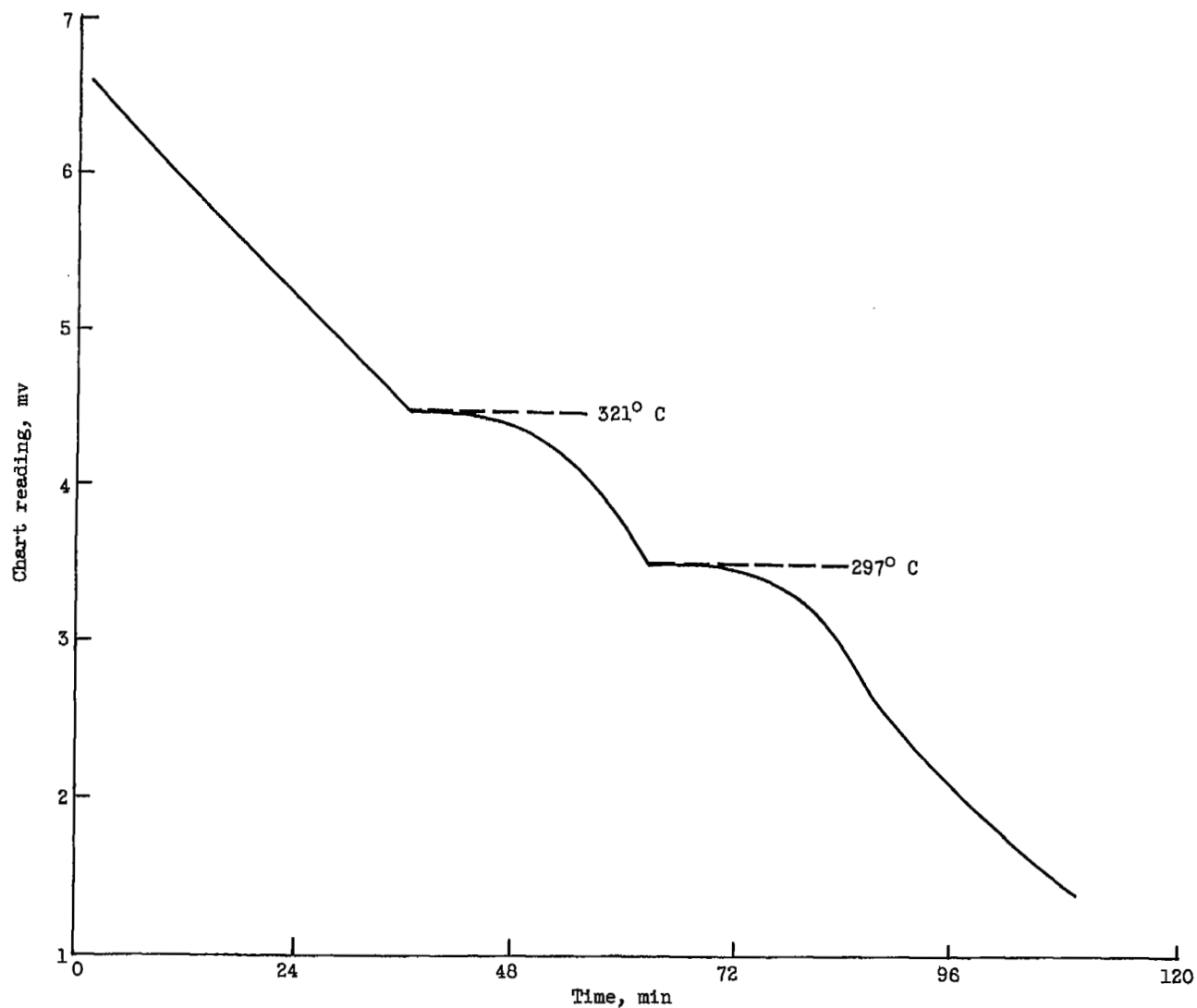Figure 1. - Furnace used for cooling curve runs. Nickel container in place.

Figure 2. - Typical cooling curve for sodium hydroxide with no additive after 103 hours at 820° C; container W-9.
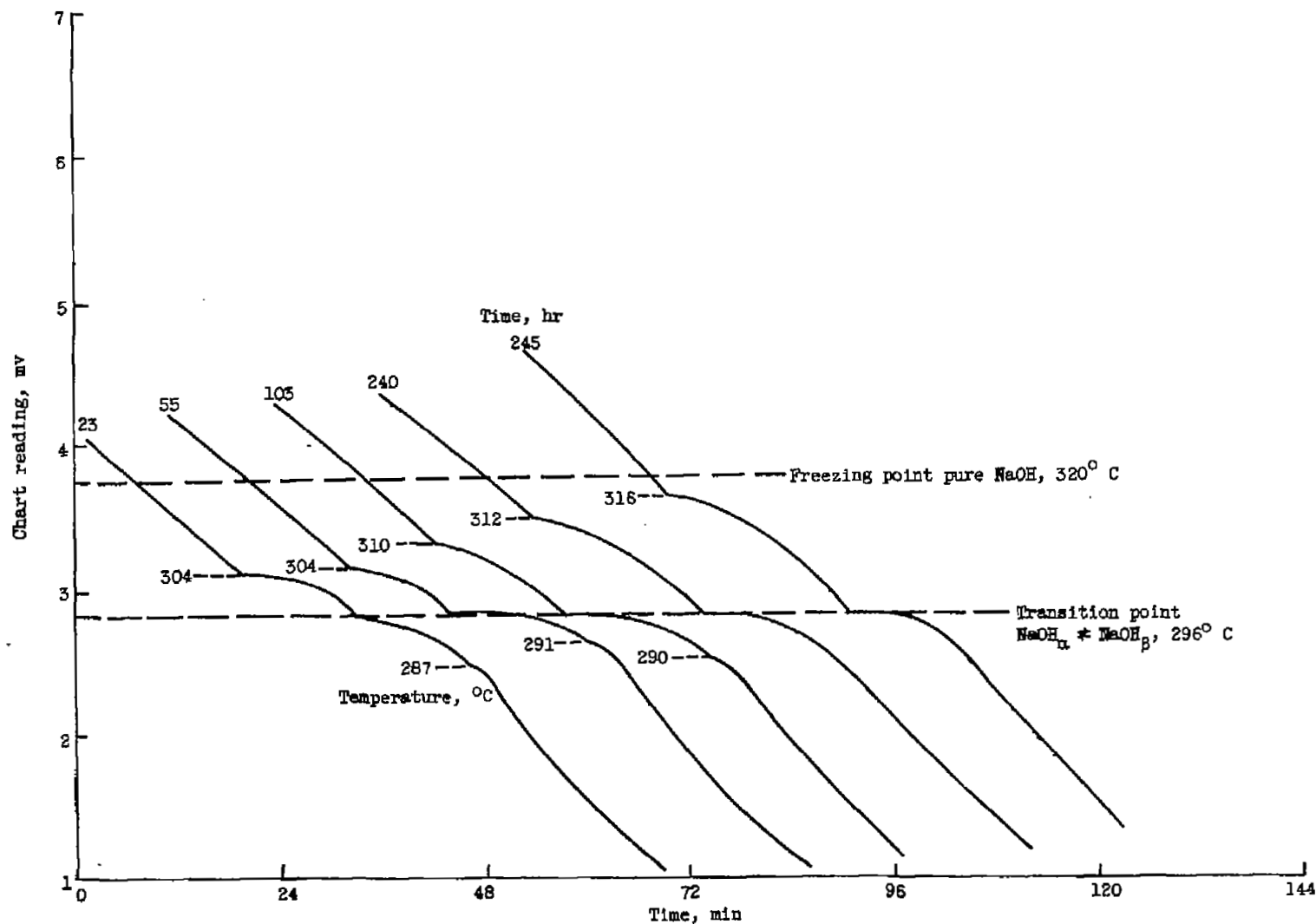
Figure 3. – Cooling curves for melt containing 10 percent chromium after various times at 820° C; container W-12.
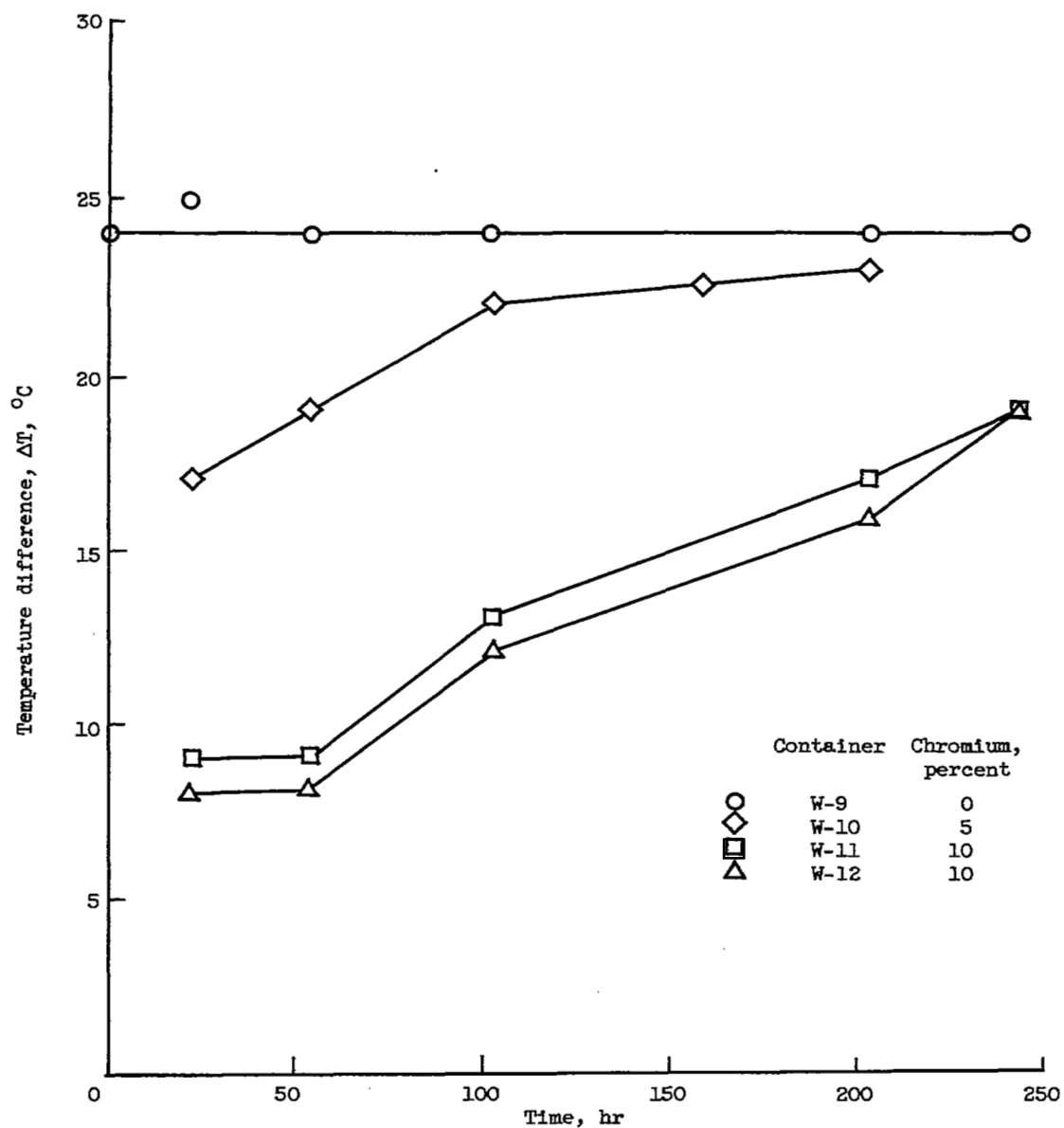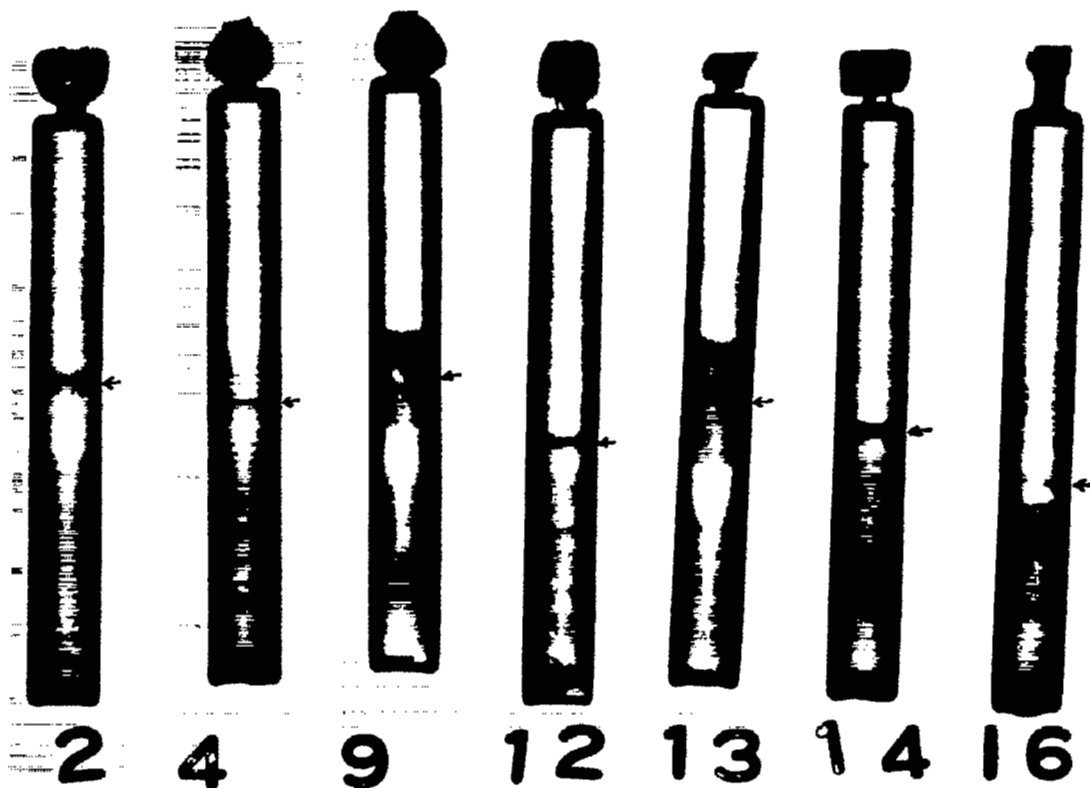
Figure 4. - Change in temperature difference (freezing point minus transition point) with time at the reaction temperature.

	Chromium, percent	Time at temperature, hr
2	0	96
4	5.8	96
9	0	245
12	10	245
13	0	240
14	10	240
16	20	240

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Figure 5. - X-ray shadowgraphs of containers showing mass transfer deposits.